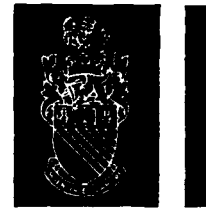R/D 5359-CH-01.F

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ADSORPTION OF WATER ON SURFACE ACOUSTIC WAVE GAS SENSORS

Final Technical Report by

Christine G.Fox and John F. Alder

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United States Army

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
London, England

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Department of Instrumentation and Analytical Science,
University of Manchester Institute of Science and
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Surface acoustic wave sensors (SAWS) respond to mass adsorbed onto chemically specific coatings put upon the acoustic wave transmission path. Target gas response is perturbed by naturally present atmospheric water vapour. This work aimed at measuring carefully the response of two particular coating materials, poly(vinyl pyrrolidone), (PVP) and FPOL (a polyfluorinated polyol). These were chosen for their particular responsive behaviour towards water (PVP) and phosphonate esters (FPOL) typified by dimethylmethyl-phosphonate (DMMP). From the water adsorption isotherms measured at 30 and 40°C, a mathematical function would be deduced to describe the response behaviour of the SAWS

over a range of relative humidity (RH) (5 to 85% RH). Using similar isotherm data derived for DMMP, a correction algorithm could be deduced to correct the SAWS output response for water vapour interference when targetting DMMP in a natural atmosphere.

The work has shown that PVP and FPOL respond reversibly to water vapour, over the range 5-85% RH at 30 and 40°C. The isotherms are qualitatively described by classical adsorption theories and a mathematical relationship relating RH to SAWS response can be derived for PVP and FPOL, over a limited range.

Much work was undertaken to determine the best design of SAWS oscillator circuit, method of variable relative humidity generation and method of SAWS coating. A circuit based on RS560C amplifiers yields stability better than 1 Hz/4 min and 5 Hz/sec for microsensors systems 157 MHz dual SAW devices, without temperature compensation in 50% RH air at 30°C. Coating methods utilising a fine hair brush or an air brush were found to be the best out of a range of methods essayed.

Table of Contents

FINAL REPORT: ADSORPTION OF WATER ON SAW GAS SENSORS

1. Introduction

1.1   SAW gas sensors rely on the adsorption of the target analyte species onto a chemically selective coating placed on the surface of the SAW device. Changes in the viscoelastic properties of the substrate cause a change in the propagation velocity of the SAW and, as the geometrical pathlength remains the same, the time which it takes a wave to traverse the path between the launching and receiving electrode on the surface. This change in delay time is equivalent to a phase difference between the electric field on the launch electrode, and that appearing at the receiving electrode as the SAW is transduced into an electromagnetic disturbance. When the SAWS is made the frequency determining element of an oscillator circuit, this phase delay can be converted into a frequency change. It is important therefore to have a stable oscillator circuit and sensitive frequency measurement system in order to measure these changes accurately, precisely and over a long period (years). Using high quality counters with stability better than 10^{-7} of the measured frequency per year and better than 10^{-9} per month, this can be achieved. The oscillator employed was designed by one of the authors and Mr.Nacer-Ddine Rezgui and is described in section 2 of this report.

1.2   The quality of coating applied to the sensor is also important. Many attempts have been made to coat piezoelectric and SAW sensors using different techniques including spray coating, evaporative deposition, spin-coating, brushing and dipping. The particular devices used in this work were 158 MHz dual delay lines of dimensions approximately 2mm by 4mm and were on the same silica plate of approximately 5mm square. Attempts using various methods were made to coat these devices, and of all, a fine brush was found to be the most suitable with a model maker's air brush as an alternative approach. The work was carried out by Mr.Akintunde A. Bellow with one of the authors and is described in section 3 of this report.

1.3   Undoubtedly the most serious problem in the development of SAWS for gas sensing is the adsorption of water vapour from the atmosphere. Water is ubiquitous and in the atmosphere at quite high levels (5-10000 ppm [in this report, ppm means parts per million by volume]). It is thus present in concentrations 4-5 orders of magnitude greater than the concentrations at which some organo-phosphonates are toxic to man. The problem of spurious response due to water adsorption is therefore considerable. Three separate approaches have been made to overcome the problem: preseparation of water vapour from target gas: hydrophobic, target specific coatings and mathematical correction of the water vapour interference to the output of the target selective SAWS. This was the main aim of the present programme undertaken by Dr.Clare J. Dudman, Miss Christine G. Fox and Dr.J.F.Alder. The approach taken was to measure the water adsorption isotherm on PVP and FPOL coatings and determine the relationship between the SAWS response and the partial pressure of water vapour at various temperatures. The work then proceeded to the measurement of DMMP and diisopropyl methyl phosphonate (DIMP) adsorption isotherms, which is ongoing. An attempt was made to relate the observed response characteristics to accepted mechanisms of adsorption behaviour, in order to base the response function derived empirically on a realistic mechanistic model. This work has been described as it developed in the Periodic Progress Reports numbers 1-4, and is brought together in section 3 below. The design and optimisation of the rig to generate reproducible atmospheres at accurately known relative humidity and temperature is a considerable task and took up more time than anticipated, but the figures quoted can be taken with considerable confidence.

2.   An RF Oscillator for 158 MHz SAWS (Nacer Odine Rezgui and J.F.Alder)

2.1   The surface acoustic wave sensors (SAWS) consist of a small slab of polished piezoelectric material on which two sets of interdigital microelectrodes have been microfabricated at each end (Figure 2.1)(Microsensor Systems. Fairfax, Va. USA). One set acts as a transmitter and the other as a receiver of acoustic energy waves. When these two sets are connected to a radiofrequency (RF) voltage of the appropriate frequency, a mechanical Rayleigh wave is generated in the piezoelectric substrate. The Rayleigh surface wave propagates from the transmitting set of electrodes across the surface to the receiving set of electrodes, where the mechanical energy is converted back into an electrical RF voltage.

2.2   Surface acoustic waves are elastic displacements propagating along the surface of the elastic substrate, where amplitude decays exponentially with substrate depth (1-3). The propagating velocity of a SAW is determined by the elastic, dielectric, piezoelectric and conductive properties as well as the mass of the surface layers of the substrate. When one of these properties is changed the SAW characteristics will also change. What makes SAW devices attractive for gas analysis is indeed the fact that most of their energy is confined to a region very near the top surface upon which they are generated, about one acoustic wavelength i.e. at 158 MHz, less than 20 μm. Any material contacting the top active surface of the SAW device will produce an alteration in the Rayleigh wave amplitude and velocity. The most sensitive response is obtained when the SAW device is used as a delay line oscillator. In this case the two transducers (interdigital electrodes) are connected to each other through an RF amplifier. In this configuration the device will generate a characteristic frequency which is determined by the spacing between the interdigital electrodes and the Rayleigh surface wave velocity (1).

$$f_0 = v_0/\lambda_0 \qquad (1)$$

where v_0 = surface wave velocity.
and λ_0 = acoustic wavelength.

Any small perturbation in the viscoelastic properties of the surface due to absorbed species will produce a change in the resonant frequency. In practice.
a thin layer (less than one acoustic wavelength) of selective material is coated onto the transmission path, and changes due to gaseous adsorption and desorption onto this are monitored.

2.3   The SAW device is coated with a selective reagent, which is deposited on the transmission path and interacts with the analyte. This will affect the SAW amplitude and velocity, which will, in turn, affect the SAW device resonant frequency (4). The resonant frequency of oscillation of the associated circuit is chosen to be monitored because it is easier to measure with precision than the amplitude of the voltage output. From Auld's equation (5), which describes the fractional change in wave velocity for a thin film, an expression for the change in resonant frequency due to perturbation in the wave velocity by a chemical interface has been derived for "soft" polymer selective chemical coatings:

$$\Delta f = (k_1 + k_2)f^2 h \rho \qquad (2)$$

where k_1 material constant for the piezoelectric substrate

k_2 material constant for the piezoelectric substrate

f resonant frequency

$h\rho$ mass per unit area of the coating film

h is the coating thickness and

ρ its density

"soft" describes the viscoelastic properties of the coatings typically used for detection work (e.g. typical gas chromatography coatings). This equation therefore relates a frequency change Δf to a change in mass, ΔM, of the coating if the surface area, A, remains constant, as $h\rho = \Delta M/A$. Gas absorbed into or onto the coating will cause a change in the circuit oscillation frequency.

2.4   A SAW delay line oscillator consists of a wide band RF amplifier having gain, and a feedback network, which is the delay line (SAW device), connected in a closed loop such that a positive feedback from the output of the amplifier is fed back to its input through the delay line. The oscillation criterion is met when the phase delay is an integral multiple of 2π and the gain exceeds unity. The electronic system consists of two identical delay line oscillators as shown in Figure 2.2. One delay line is used for sensing and the other for temperature, pressure and interference compensation. The acoustic path of the sensing delay line is covered with a selective chemical coating. Absorption of a gas occurring at the gas selective surface causes a velocity change in the acoustic signal, leading to a phase shift between the input and output signals of this delay line. This phase shift results in a frequency change in the oscillator frequency f_1. The other delay line oscillator may be uncoated, or differently coated and used as a reference, having a frequency f_2. The frequencies obtained from each oscillator are connected to a mixer and an active low pass filter (ALPF, Figure 2) selects the difference frequency f_3 of f_1 and f_2, which is a measure of the gas concentration.

2.5   The dual SAW delay line oscillator was built in the same module using a double-sided printed circuit board. Each delay line comprises two stages of RS 560C (RS Components part No.303-214, RS Components, Stockport, Cheshire) in series (Figure 2.3). The RS 560C is a wideband RF amplifier providing a gain of 35 dB and operating up to 200 MHz. This gain is significantly greater than the insertion loss of the delay line typically 10 dB. The output of the amplifier is fed back to its own input through the delay line and the circuit oscillates at the resonant frequency of the delay line (Figures 4 and 5). The mixer and the active low pass filter (ALPF) were built also in the same module using a double-sided printed circuit board. The minicircuits TFM2 double balanced mixer (Dale Electronics, Camberley, Surrey) was used with a NE592N video amplifier (RS Components Part No.301-583) configured as an active low pass filter, to pass the difference frequency between the two delay line oscillators. The filter cut off frequency was 5 MHz. The assembly connected together and switched on showed a drift of 1 Hz/4 min and a short-term stability of $\pm$ 5 Hz/sec. for both SAW delay line oscillators, due to slow thermal changes in the substrate and amplifiers. The two SAW delay line oscillators were affected similarly in environmental chamber tests over the temperature range $-46°$ to $+82°C$ with a temperature coefficient of about 2 kHz/°C. The output of the ALPF which is the difference of the two channels is less affected and shows good stability (less than 1 kHz/°C) over the temperature range -46 to $+82°C$ and less than 65 Hz/°C over the range $14-46°C$. Harmonic and spurious signal outputs were monitored on a Hewlett Packard 8590A spectrum analyser (Hewlett Packard, Stockport, Cheshire) and the spectrum shown in Figures 2.4 and 2.5 for the two

oscillators running simultaneously. The measured bandwidth (-3dB) of the 158 MHz output was 733 kHz. which compares favourably with the calculated value of 711 kHz. The spurious and harmonic levels were so low as not to interfere with the counting characteristics of the frequency counters employed for this work (Philips PM6673. which are specified to 120 MHz but actually respond to 158 MHz if the input voltage is high enough, or Racal Dana, 9921 counters). The 158 MHz oscillator output voltage was typically 300mV p-p into 50 ohm.

2.7   The examples of this circuit have been in continuous use in the laboratory for more than one year and have proved most useful and reliable.

<u>References</u>

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         B.A.Auld. Vol.2. Ch.12. Wiley-Interscience. New York 1973.
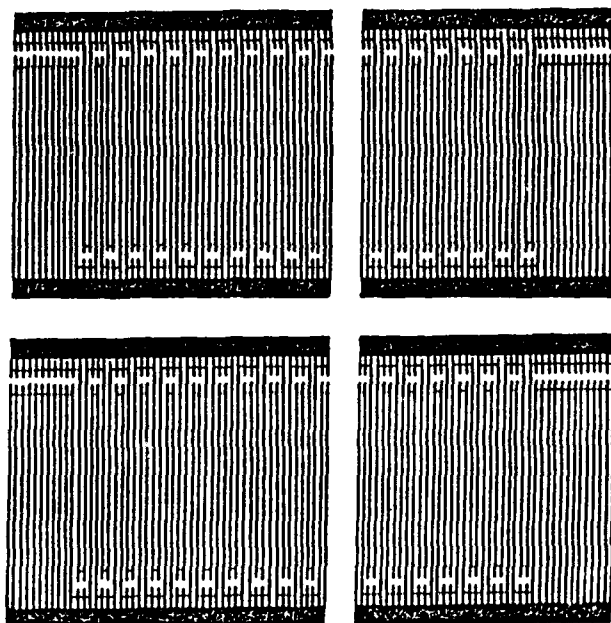
Substrate STX quartz

IDT 1: 100 pairs of split-electrodes (2 mm)

and a reflector of 60 solid electrodes (0.3 mm).

IDT 2: 75 pairs of split-electrodes (1.5 mm)

and a reflector of 70 solid electrodes (0.4 mm).

Space between the two IDTs: 0.2 mm.

Centre to centre distance of the two IDTs: 1.95 mm.

Aperture   : 1.4 mm.

Centre to centre distance between two electrodes : $\lambda/4$ (5 m).

    20 m.

v : 3158 m/s.

f : v/λ 158 MHz

Figure 2.1 - 158 MH dual SAW device.

SAW DEVICE

WIDEBAND
RF AMPLIFIER

WIDEBAND
RF AMPLIFIER

TEST POINT

TEST POINT

F 1

F 2

DOUBLE BALANCED MIXER

IF

ALPF

DIFFERENCE FREQUENCY

OUTPUT

240
V AC

REGULATED
POWER
SUPPLY

± 6
V DC
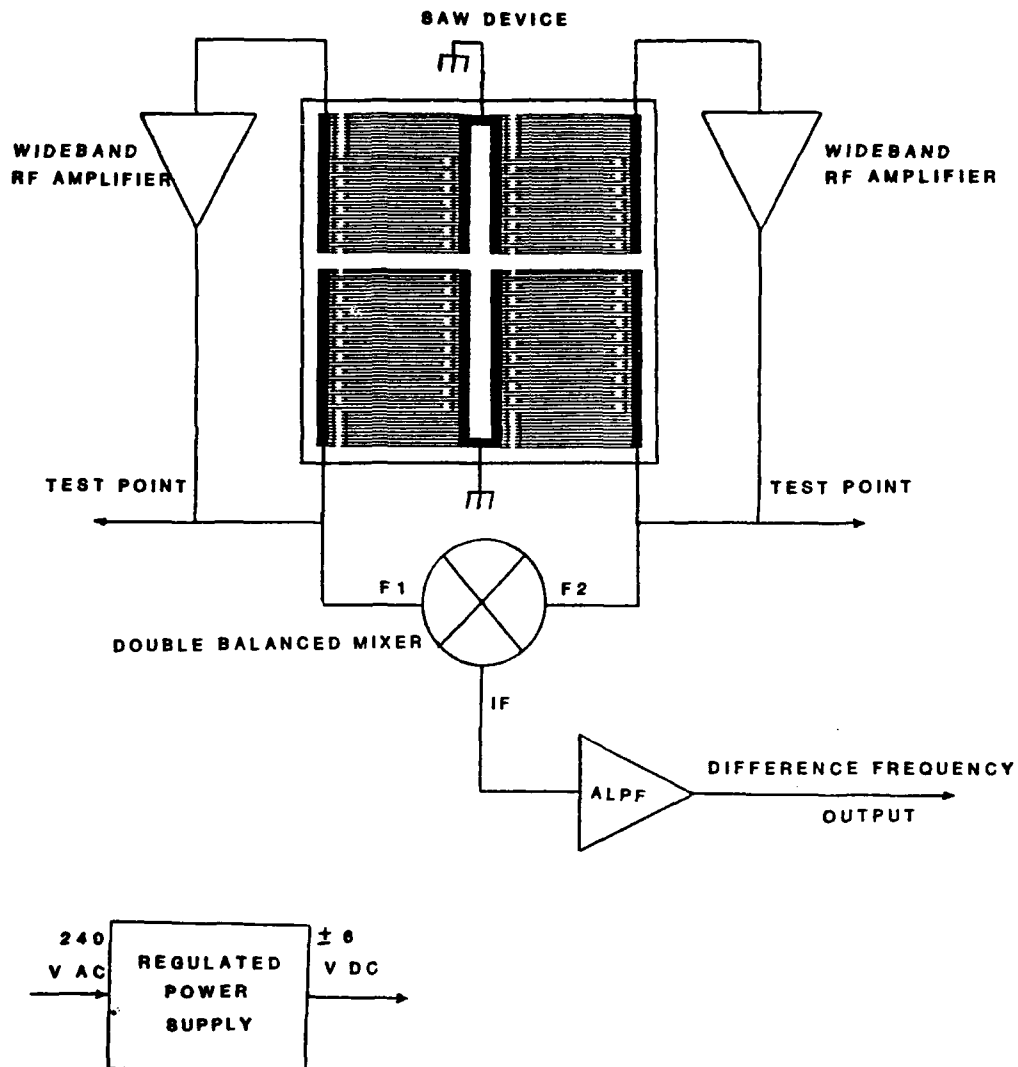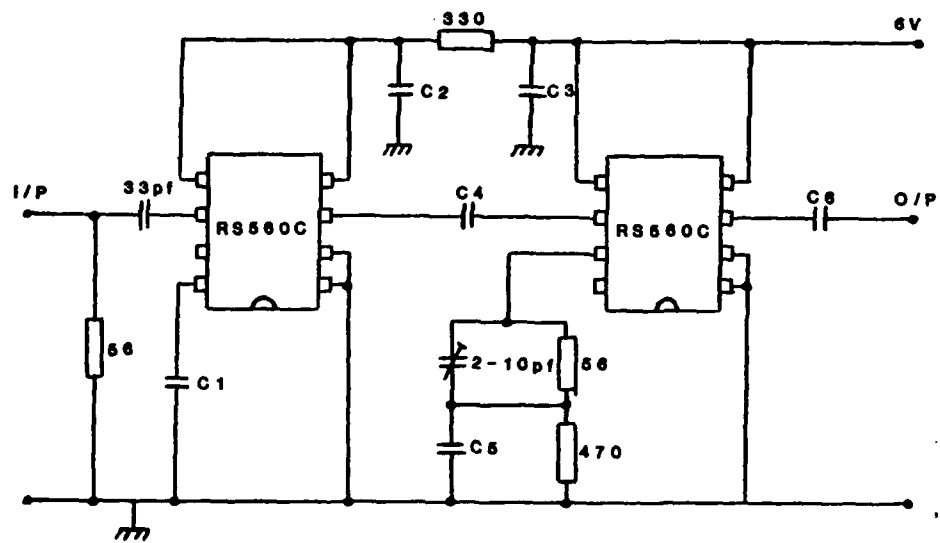
Figure 2.2 - 168 MHZ dual SAW delay line oscillator
system diagram.

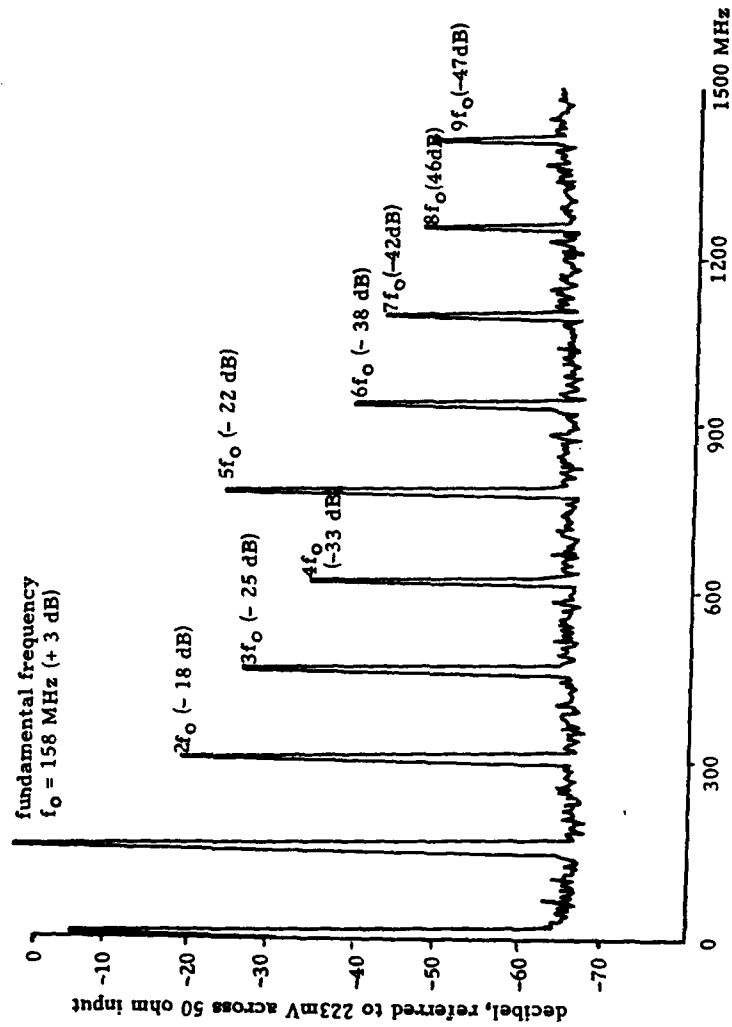Figure 2.3 – RF amplifier used for the SAW dual delay line oscillator.

Figure 2.4 Spectral output of channel 1 showing the fundamental frequency and its harmonics (Attenuation 10 dB)
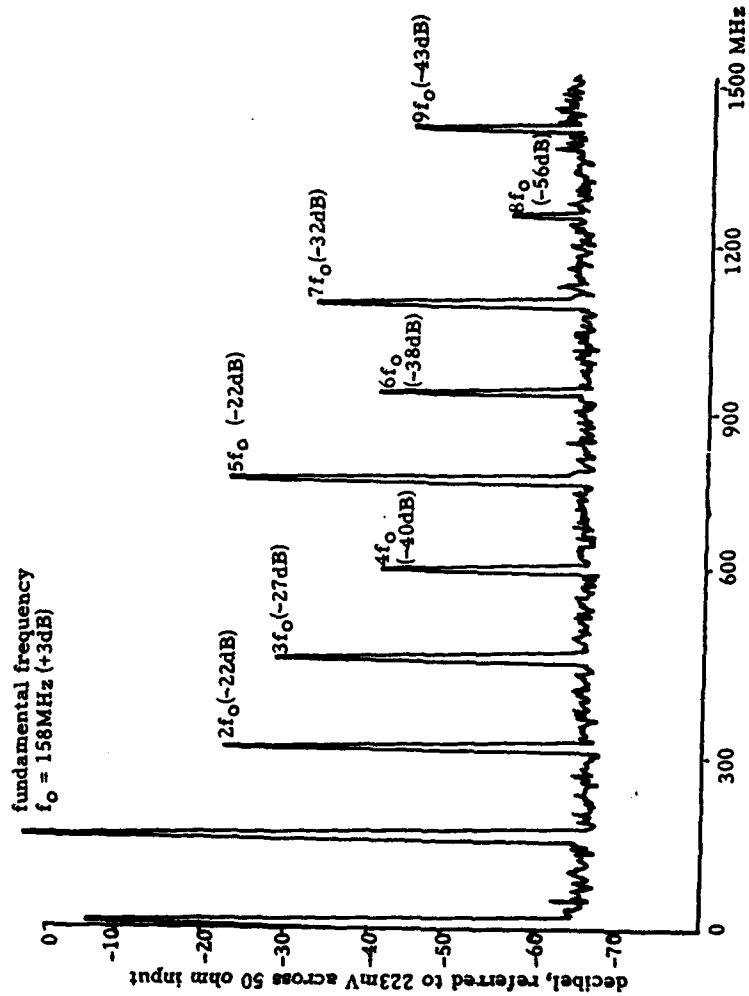
Figure 25 Spectral output of channel 2 showing the fundamental frequency and its harmonics (Attentuation 10dB)

3. **Coating Techniques for SAWS** (A.A.Bello, C.J.Dudman and
    J.F.Alder)

3.1   A number of methods have been described for coating both bulk
piezoelectric crystal and SAW devices. These include: painting with a brush,
painting with a swab, dipping, spraying with both a spray gun and an air brush,
dropping by microsyringe, spin-coating, Langmuir-Blodgett film transfer and,
sputtering. In this project the application of organic films was of interest and
the specific techniques for the application of inorganic coatings were ignored.

3.2   The widespread popularity of painting the coating on with a brush
is due to its versatility. Brush application can be used in an almost unlimited
number of conditions and situations. The operator is to a large degree in control
of the brush movement and the amount of material applied. The use of fine
brushes to apply coatings to both SAW devices and bulk piezoelectric devices
has been described by several workers. Paint brushes are available in a range
of sizes and for the coating of the small areas used here, the pencil brushes and
liners were ideal.

3.3   Although swab application is not terribly refined and is less
versatile, it may be considered a specialised brush application method. The use
of disposable cotton ball ("Q-Tips") designed for cosmetic applications, has been
very common in bulk piezoelectric crystal work. We have used it in this
department for many years and with considerable success. For the very small
devices used in this work however the swab was found rather too clumsy to be
usefully employed.

3.4   Dipping the SAW device involves rapid immersion and removal
of the SAWS to be coated, in a solution containing the coating. The SAWS is
then dried either at ambient temperature or in an oven. With this method, uneven
film thickness may result due to draining and the method is also limited that
it does not offer a great deal of control over either the amount of coating applied
or the area coated. In the particular case of the 158 MHz devices supplied by
Microsensor Systems, a further problem arose. The device came already mounted
in a holder and could not be removed. This meant that the entire holder had
to be dipped into the coating solution if one was to have any hope of only coating
one half the device. In truth, the capillary film which forms and brings the
meniscus up the side of the device meant that one could not readily coat only
one side and often, the meniscus travelled across the entire silica substrate and
coated both sides. This effectively precluded the method of dipping in this
particular application.

3.5   A similar comment applies to spin-coating techniques. It is
relatively easy to spin-coat a device where only one active area is being coated.
In the particular case of the Microsensor Systems dual-SAWS, however, one could
not coat just one half of the device by this method as masking was precluded
due to the considerable fragility of the SAWS and its connecting wires. For all
the attractions of spin-coating, the technique could not be applied in this particular
case.

3.6   Dropping by microsyringe onto the surface has also been employed
by many workers and remarkably gives not very good results. The drop tends
to spread and evaporate from the outer surface leaving a ridge of material at
the outside of the evaporating film. This causes unevenness of coating which
it ultimately difficult to rectify by subsequent thermal treatment. In our
experience, it is not a very good approach.

3.7   Spraying the materials on with an air brush or similar aerosolisation
device, has been quite successful and with practice, the operator can carefully

coat specific areas of the device with typical modelmaker's air brush instruments. It can clearly not be applied to every coating but was found useful in the PVP and FPOL application procedures.

3.8   Langmuir-Blodgett films can be laid on liquid surfaces and transferred to devices like SAWS. We were not able to make Langmuir-Blodgett films and did not have ready access to any troughs to try out this technique. In the amount of time available for this particular part of the programme it was not possible to develop this technology and one also anticipated problems with meniscus creep as had been found in the conventional dipping procedures. It is perhaps worthwhile considering this for future applications although there are many problems associated with the method and it is practically difficult and expensive to put into action.

Experimental Approach

3.9   Two coatings and a number of solvents were essayed in this work. PVP and dicyclopentadienyliron (ferrocene) were employed. Ferrocene was employed to permit quantitative assessment of the amount of material put onto the SAWS. The ferrocene applied could later be removed and determined colorimetrically using potassium thiocyanate as a reagent. In this way the total amount applied could be determined. Both the coatings could be inspected visually using an optical microscope and a qualitative assessment of the coating made. In this way, both quantitative and qualitative estimation of the coating procedures was undertaken.

3.10   Only the work describing the more successful paint brushing and air brushing techniques will be described here. The paint brush employed was size 000 which consisted of a few camel hairs. The air brush employed was a "Devilbis" sprite device and consisted of a spray gun with attached spray container connected to a gas propellent can via a hose. Both the gas supply and the flow of coating solution were managed by a dual action control button. Downward movement of the button controlled the gas pressure whilst horizontal backward movement metered the flow of coating solution. The device also employed a lockable camring allowing a set flow rate of the coating material. Coating application initially required setting the camring to the position which gave the optimal flow rate for the solvent coating mix at the gas pressure applied. The laying down of coatings of the required dimensions was practised (lines of 2mm width) on dummy devices (microscope slides). Manual spraying was eventually possible without the use of stencils or masks.

3.11   A very extensive study was undertaken over a four-month period. In summary, for the PVP coatings there was found to be some correlation between the controllability of application and the solvent used in the coating solution. In general, the best control was achieved by using PVP in dichloromethane. Coating solutions made up using propan-2-ol as the solvent seemed to be the least controllable when applied. The coatings of PVP in methanol were marginally more controllable than those in propan-2-ol. Relationship between the quality of the film and the solvent coating mixture was the reverse of that described for the solvent versus controllability. Films applied using propan-2-ol as the solvent were more even than those using methanol. The films that were applied with dichloromethane tended to be the least even and the most contoured. This relationship between film quality and controllability appears to have been predominantly governed by the solvent coating mixture. The solvents which evaporate quickly, i.e. acetone and dichloromethane seem to allow better control over the area to be coated whereas the slow evaporating solvents, particularly propan-2-ol, although giving only a limited control over application tended to give rise to more uniform films on evaporation.

3.12   The correlation between the techniques used and the controllability of application was less pronounced. Painting gave good control with all of the coating solvent combinations. When PVP coating is dissolved in dichloromethane and methanol were applied by air brush, a good control was observed. The best combined control of application and general film quality was achieved by the application using an air brush and PVP coating dissolved in methanol. The quantitative measurements using air brush application revealed that a mean of 0.74μg with a relative standard deviation of 27.7% was achieved. This should be compared with the brush application where the mean mass of coating deposited per application was 0.24μg with a standard deviation of 18.3%. The number of replicates was 5 and 10 for the air brush and brush coating respectively.

3.13   It is clear from this work therefore, that both air brush and brush application of the coatings is the most useful way of putting on materials to the SAW device. The problem with the air brush for occasional coating procedures which is the situation in our work, is the considerable complexity of setting up the air brush and working it. Also, the large volumes of materials used are rather wasteful and it is felt that the air brush is more suited to large scale production rather than the occasional one-off. For our work, the fine paint brush gives a reproducible coating of the right mass which is quite reproducible. After application of the PVP in propan-2-ol, the SAWS is put in an oven at 40° for 12 hours to permit complete evaporation of the solvent and allowing the film to spread to an equilibrium position. For the FPOL, the solution employed was 0.1% of the polymer in methanol and the application and treatment was done in the same manner.

4.   **Measurement of the Water Adsorption Isotherms on PVP and FPOL**

4.1   The work described in Periodic Reports 3 and 4 has been continued to obtain adsorption isotherms for PVP and FPOL. In the last period, the main thrust has been to determine the degree of hysteresis in ascending and descending humidity studies and to monitor the effect of change in temperature. In hysteresis studies, FPOL was chosen for study over the range approximately 10% to 75% relative humidity at 30°C. FPOL was also chosen for the different temperature studies. In other work PVP and FPOL were studied for their adsorption characteristics. The FPOL solution was made up at 1% w/v in methanol and the PVP solution was at 0.1% w/v using propan-2-ol as the solvent. Solutions were brushed onto the surface of the SAWS on either, or both sides of the device depending upon the experiments under way. When only one side was coated the side having the lower operating frequency uncoated, was chosen as the one to be coated. This resulted in a greater difference in frequency between the coated and uncoated side and meant also that the difference would increase as the water was adsorbed onto the surface. This overcame any problems that would otherwise occur if the frequencies of the two sides of the oscillator circuit became equal to each other. The operating frequencies of both sides of the oscillator were recorded once equilibrium was reached after exposing the SAWS to dry air (RH better than $\pm$ 2%).

4.2   Polymer solution was applied with a fine brush (see Section 2). Three strokes of the brush coated one side of the SAWS. The solvent was allowed to evaporate and the SAWS was coated again. This process was repeated up to five times for the less concentrated PVP solution but no more than twice for the more concentrated FPOL solution. The SAWS was then placed in an oven at 40°C for 12 hours to allow the solvents to completely evaporate. After this time the SAWS was again exposed to dry air and the frequencies were recorded once equilibrium had been attained. (The SAWS were always dried to constant frequency to ensure that solvent evaporation and bleed was complete). 12 hours had been shown in previous studies to be a useful time over which to do this. The difference in frequency between the first and second readings was attributed to the surface coating. The PVP coated SAWS had polymer on both sides of the device and the coating level was equivalent to a frequency change of 73 kHz and 18 kHz on the two sides respectively. One FPOL coated SAWS coated on one side had a frequency change of 64 kHz. The frequency changes proportional to the added mass, and for a given SAWS is a useful way of describing the surface loading. It can be translated into mass if one assumes certain properties and characteristics of the coating. But for a given SAWS device and a given coating, the frequency change on coating is itself a useful way of describing the loading.

4.3   The isotherms were produced by exposing the coated SAWS in the test rig as described in the previous Periodic Reports. The same procedure was used for data obtained at 30° and 40°C. The SAWS was first exposed to dry air (RH $\pm$ 2%) and the frequency recorded once the signal became steady. Wet air was then passed over the SAWS and the new frequency recorded when the signal became steady. Each reading took a considerable time to stabilise due to the very slow response time of the test rig. At each change in concentration of water vapour the whole system has to re-equilibrate and stabilise and this took a period of anywhere between 15 minutes and 1 hour. All of the data presented below took weeks to compile, a typical single run from low to high relative humidity would take easily one working day and in order to repeat the results to obtain the standard deviations took many days. The data for the hysteresis experiments took three weeks to obtain. The six different test humidities were generated from five saturated salt solutions and pure water. The final relative humidity of the atmosphere was monitored using a RH sensor

Table 4.1

Coating	Material Side 1	Side 2	Temperature	RH(%) generated from: Saturated Salt Solution					Water
				LiCl	$MgCl_2$	$Mg(NO_3)_2$	NaCl	KNO_3	H_2O
PVP	73kHz	18kHz	30°C	15	26	41	58	73	77
FPOL	63kHz		30°C	11	24	39	57	70	78
FPOL			30°C	9.5	23	38	55.4	69.7	76.4
				10	26	40.4	54.9	72.4	76.2
FPOL			40°C	9.8	22	34.3	49.4	–	–

and readout which was calibrated in both static and flowing systems and cross-checked with another meter which was calibrated against a reference standard in another laboratory. We are quite confident that the relative humidities and partial pressures described are accurate to within about 1% and the relative standard deviation of the results upon any given set of experiements will be less than about 2%. The conditions for the experiments reported in this Final Report are outlined in Table 4.1 below.

As mentioned above, the frequencies are recorded with humid air and then on every occasion dry air was passed over the SAWS until a steady reading is obtained. The change in frequency going from dry air to wet air or wet air to dry air was assigned a positive value if a decrease in frequency was observed on increasing the humidity and if there was an increase in frequency when the humidity was decreased. This is because one is looking for a positive frequency change on loading in order to associate a positive change in concentration of gas in the atmosphere to a positive change in frequency.

4.4   Tables 2-5 contain data obtained on exposing the PVP and FPOL coated SAWS to air of different relative humidity. They display the frequency changes observed and the vapour pressures corresponding to the various relative humidities.(Note: the abscissae are graduated in partial pressure of water/mm Hg (P_{H_2O}) which is equal to [(RH/%)/100] x sat.vapour pressure of water at that temperature].Figures 4.1 to 4.4 show the results of these tables graphically, where change in frequency is plotted against the partial pressure of water.

Table 4.2   PVP coated SAWS at 30°C

Relative Humidity /(%)	Side 1 $\Delta f/(kHz)$	Side 2 $\Delta f/(kHz)$	P_{H_2O} /(mm Hg) (RSD ≈ 2%)
14.75	2.47 (± 0.250)	0.811 (± 0.121)	4.69
26	3.057 (± 0.189)	1.798 (± 0.260)	8.27
41.5	5.952 (± 0.560)	2.614 (± 0.190)	13.20
58	9.118 (± 1.398)	4.235 (± 0.260)	18.44
73	11.366 (± 0.909)	8.197 (± 0.492)	22.97
77	14.352 (± 1.554)	9.488 (± 0.540)	24.48

Table 4.3   FPOL coated SAWS at 30°C

Relative Humidity /(%)	Side 1 Δf/(kHz)	Side 2 Δf/(kHz)	P_{H_2O} /(mm Hg) (rad ≈2%)
11	2.305 (± 0.404)	1.039 (± 0.149)	3.45
24.25	3.676 (± 0.373)	1.508 (± 0.128)	7.71
39.375	6.450 (± 0.602)	2.476 (± 0.209)	12.52
55.3	8.788 (± 0.277)	3.851 (± 0.248)	17.58
70	11.9 (± 0.323)	5.06 (± 0.406)	22.26
78.4	12.214 (± 0.324)	5.977 (± 0.211)	24.93

Table 4.4   FPOL coated SAWS at 30°C.   Testing for hysteresis in the system

Relative Humidity /(%)	Side 1 Δf/(kHz)	Side 2 Δf/(kHz)	P_{H_2O} /(mm Hg) (rad ≈2%)
9.5	1.005 (± 0.120)	-0.427 (± 0.095)	3.02
23	1.553 (± 0.125)	-0.207 (± 0.132)	7.31
38	3.753 (± 0.282)	0.761 (± 0.163)	12.08
55.4	5.962 (± 0.276)	1.861 (± 0.141)	17.61
69.7	7.282 (± 0.499)	2.837 (± 0.219)	22.16
76.4	9.047 (± 0.319)	3.649 (± 0.238)	24.30
76.2	9.348 (± 0.282)	3.509 (± 0.314)	24.28
72.4	7.251 (± 0.255)	2.988 (± 0.212)	23.03
54.9	5.198 (± 0.406)	1.473 (± 0.206)	17.46
40.4	4.141 (± 0.163)	0.833 (± 0.159)	12.85
26	2.018 (± 0.273)	0.317 (± 0.119)	8.29
10.	1.232 (± 0.072)	-0.038 (± 0.087)	3.18

Table 4.5   FPOL coated SAWS at 40°C

Relative Humidity /(%)	Side 1 Δf/(kHz)	Side 2 Δf/(kHz)	P_{H_2O} /(mm Hg) (rad ≈2%)
9.8	3.016 (± 0.149)	0.458 (± 0.182)	5.43
22	3.491 (± 0.114)	0.989 (± 0.173)	12.17
34.3	4.312 (± 0.237)	1.573 (± 0.272)	18.98
49.4	7.122 (± 0.552)	2.846 (± 0.276)	27.77

4.5   Figure 4.1 shows the effect of relative humidity on change in frequency for PVP coated SAWS at 30°C. In these data the results are obtained only in ascending order of relative humidity and the feature to note is the significant change in gradient of frequency versus partial pressure of water which occurs at around 8 mm for side 1 and 16 mm for side 2. This break appears with almost all of the isotherms we have obtained and is discussed elsewhere. Significant also is the fact that the lower mass coated side exhibits better reproducibility than the higher mass coating. This seems to be also a general phenomenon and hysteresis effects are also noticeably less in cases where the mass loading is minimal. Figure 4.2 shows the effect of humidity on an FPOL coated delay line. with the other delay line remaining uncoated. In this particular example the break at around 8 mm mercury is much less pronounced and one can draw a straight line through the data points which shows a reasonable fit. One is drawn in this graph to aid clarity but there is no implication that a straight line describes the response function. The response of side 2. which is uncoated. is characteristic of an uncoated delay line, but the relative standard deviation is rather better than one would normally obtain and the exact reasons for this are not certain. Clearly the response characteristics of the quartz and gold are less affected by water vapour than the FPOL. Figure 4.3 shows the results from the careful attempt to demonstrate hysteresis effects on the crystals. In this case, the same SAWS that was used for the previous work described in Figure 4.2 was employed but exposed over a 3 week period to ascending and descending relative humidities. Great care was taken here to ensure that the response hysteresis was that of the coating if anything, and not the rig. No lines have been drawn through the data as they would confuse the issue but the data demonstrate quite well that there is no significant hysteresis in the coating, or for that matter on the uncoated side. Previous experiments we have carried out which indicate hysteresis must in some aspects either reflect the fact that the coatings take a long time to equilibrate or, and more likely, that the rig itself takes a long time to come to equilibrium. The break at around about 8 mm mercury for the gradient of the FPOL coated crystal is noticeable in these data but a portion from 8 mm mercury to 24 mm mercury shows a response which could be reasonably approximated to a straight line. This is true also for the uncoated SAWS over the region 12-24 mm mercury. Figure 4.4 shows the data from Figure 4.3 plotted as the graph obtained at 30°C (dotted line, the error bars have been omitted for clarity). Superimposed on these are results obtained in ascending order only for the same crystal exposed to air at 40°. Two things are rather noticeable. first the increase in curvature of the isotherm for FPOL and second the empirical observation that the isotherms seem to have been rotated clockwise in going from 30° to 40°C. The implication is therefore, that at the higher temperature more water is adsorbed at lower partial pressures of water and less at the higher partial pressures than those at the low temperature. The physical significance of this with regard to the mechanisms involved in the adsorption process are not totally clear but there is an indication of how to compensate for temperature changes easily if one can rotate the isotherm as a function of temperature in the correction algorithm. We have too few data to go on and clearly this is an area of considerable further interest. More discussion as to the interpretation of these data will be given in section 5 and 6.

4.6   Parallel with the work on the water vapour. a rig for testing the SAWS with DMMP and DIMP has been designed and is currently in the process of proving. Before investigating the response of the SAWS to the phosphonates in humid air. it is necessary to develop a response algorithm for the SAWS exposed to dry air containing the organic phosphonates. The rig which eventually will expose the SAWS to varying concentration of phosphonates in varying concentrations of water vapour is going to be very complex and one needs to have proved the initial parts first. The relative humidity test rig is well proven

and the proving of the DMMP/DIMP rig is now in progress. Figure 4.5 shows a block diagram of the rig in its present state of development. A humidity sensor is not used in this design as the air is maintained at a relative humidity less than 2%. One also must be aware of the possibility of contamination of the humidity sensor with DMMP and future designs will need to avoid this happening. The diaphragm pump used to circulate the air causes pressure pulses and the molecular sieve tubes and carbon filter getters, act not only as desiccants but also as pulse dampers. The dreschel bottle in Figure 4.5 (7) acts as a ballast to minimise pulses also. In this way, a pulse-free flow of air is able to pass over the diffusion tube in its thermostat bath. Calibration of the diffusion apparatus is by weight loss from the diffusion tube measured over months, and day-to-day reproducibility is checked by a GC with phosphorus detector. We are currently at the stage of being able to produce ppm and sub-ppm levels of DMMP and are just beginning the adsorption isotherm measurements. This information will be transmitted to US Army in a supplementary report, towards the end of calendar year 1989 as the work progresses (funded separately from personal research funds at present).
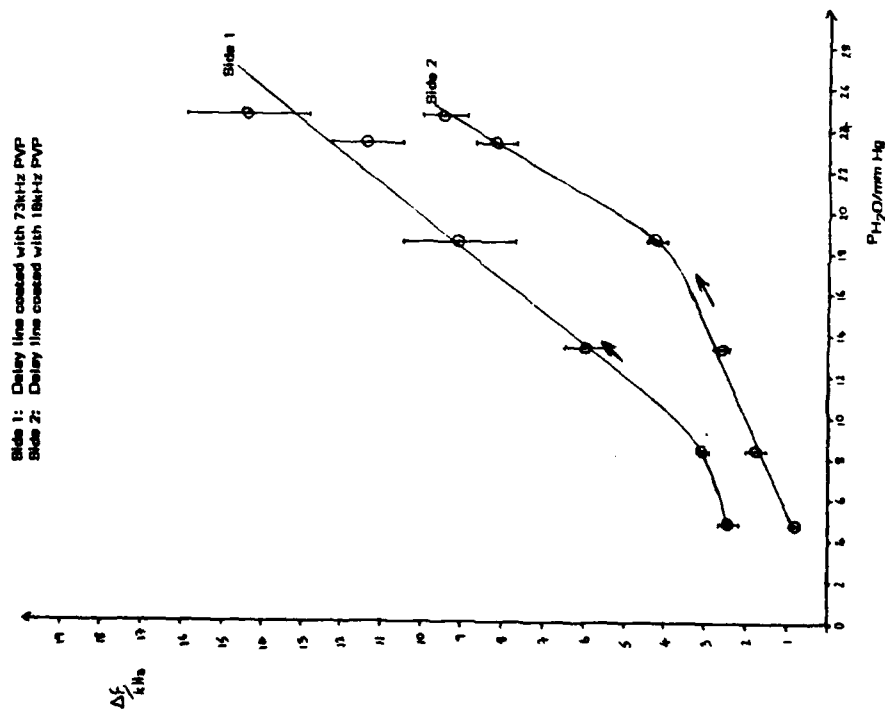
Figure 4.2

Showing the Effect of Humidity
on Change in Frequency (Δf) for the
FPOL Coated Delay Line (side 1) (63 kHz coating)
and the Twin Uncoated Delay Line (side 2) at 30°C

Slide 1

Slide 2

P_{H_2O}/mm Hg

Δf/kHz

Figure 4.1

Showing the Effect of Humidity on
Change in Frequency (Δf) for a PVP
Coated BAW8 at 30°C

Side 1: Delay line coated with 73kHz PVP
Side 2: Delay line coated with 18kHz PVP

Slide 1

Slide 2

P_{H_2O}/mm Hg

$\frac{\Delta f}{kHz}$

Figure 4.4 Showing the Effect of Humidity on change in frequency for an FPOL coated SAWB at 40° and 30°C

- - - - - 30°C
———— 40°C

Side 1: Coated with 84 kHz FPOL
Side 2: Uncoated

Side 1, 30°C
Side 1, 40°C
Side 2, 30°C
Side 2, 40°C

Δf /kHz

P_{H_2O} /mmHg

Figure 4.3 Showing the Effect of Humidity on change in frequency for an FPOL coated SAWB at 30°C

- increasing humidity from 9.5% to 76.4% RH
- decreasing humidity from 76.2% to 10% RH

Δf(kHz) = change in frequency going from wet to dry air or dry to wet air.

Error bars are standard deviation

Side 1 (coated with FPOL)

Side 2 (uncoated)
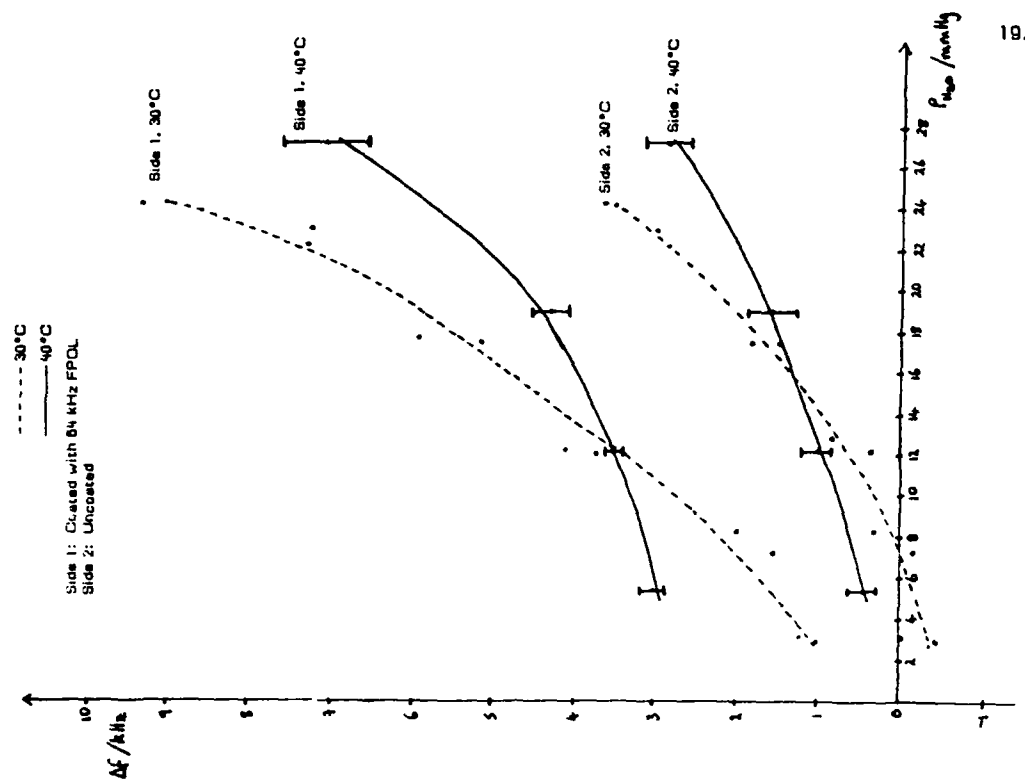
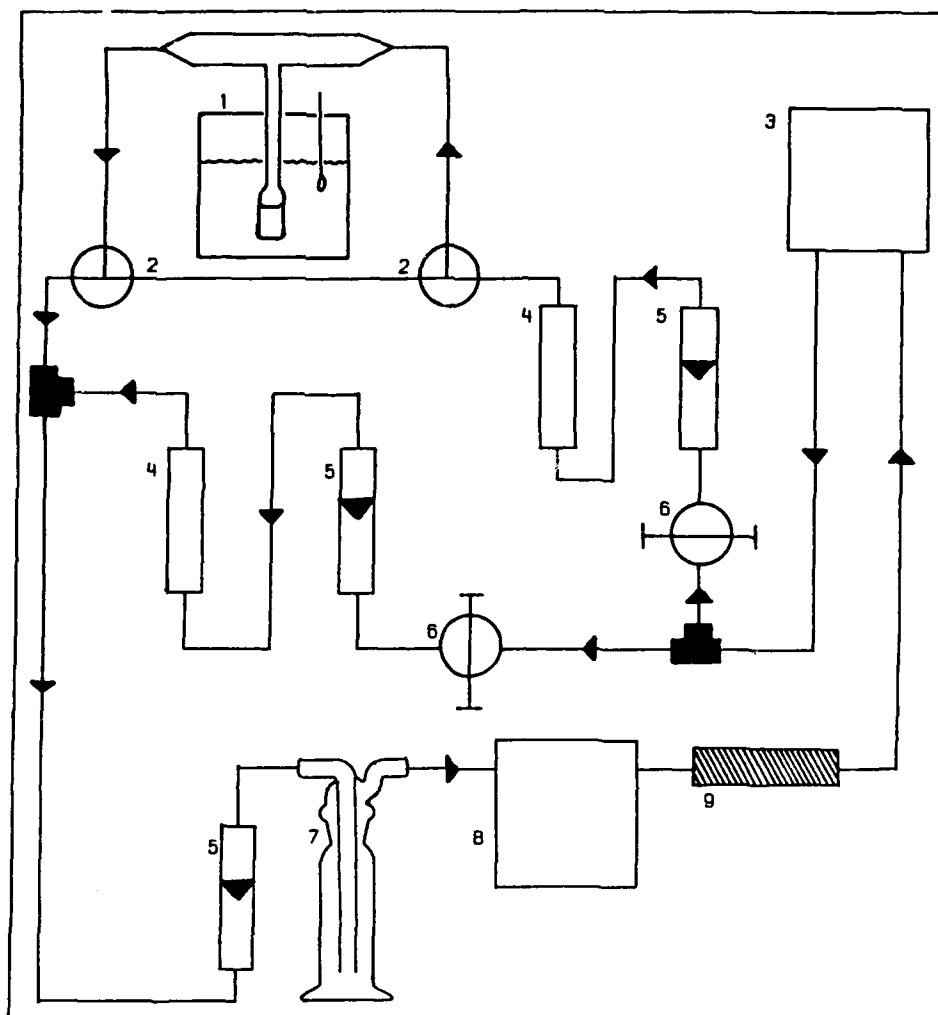P_{H_2O} /(mm Hg)

Δf (kHz)

Figure 4.5 New Rig Design for DIMP and DMMP testing at <2% RH.

1. Diffusion tube containing DIMP or DMMP in thermostat bath
2. Teflon three-way valve
3. Diaphragm pump (recirculatory)
4. Molecular Sieve 4A Desiccant
5. Flow meter
6. Flow control valve
7. Ballast
8. SAWS Oscillator Circuit
9. Carbon vapour filter (Sutcliffe Speakman ASC charcoal)

5.   Derivation of the Water Response Function

5.1   Observation of the data presented here and in the previous data presented in the Third Periodic Report particularly (Figures 7-12 in that report) indicate that the response characteristics for both PVP and FPOL to water vapour over the relative humidity range 10-75% are far from simple. There appears to be two mechanisms prevailing, one at the low relative humidities and the other at higher relative humidities, possibly associated with a complex mechanism of monolayer formation associated with diffusion of the adsorbed water into the bulk of the polymer causing swelling at the lower concentrations. Above about 50% RH with PVP and possibly at the lower relative humidity associated with FPOL, clustering begins and the dominant mechanism at the higher temperature could involve cluster formation on the surface. The onset of this cluster formation compared with the rates of diffusion into the surface and bulk regions will be affected both by the mass of material on the surface and the temperature at which these effects take place. Clearly therefore the relationship between the atmosphere relative humidity, the atmosphere temperature, the surface temperature of the SAWS and the amount of coating on the surface is going to be rather complex and dependent upon the way the particular SAWS was manufactured. One is also able to see the potential problems arising from hysteresis if the relative humidity is changed too quickly. To some extent therefore it is not possible to relate quantitatively the frequency change to the partial pressure of water vapour for any general set of conditions. Clearly, if one measures an isotherm under a given set of conditions for a given SAWS one can derive an empirical response function which indeed for FPOL could be approximated simply to a straight line at relative humidities at around ambient, as indeed they could for PVP at temperatures around 40°C. The trouble is, one would need to know what this empirical adsorption isotherm was before the coefficient for such an algorithm could be put in and the rate of change of relative humidity and the previous history of the coating would clearly have a very significant effect.

5.2   Moving to the higher temperatures makes the response function less marked for both PVP and FPOL and gives a clear indication that the best conditions under which to work from the point of view of gradient of frequency versus relative humidity is at the higher temperatures. In the case of FPOL however the situation is complicated somewhat by the change in shape of the curve.

5.3   It is therefore possible to write an empirical formula which describes any given isotherm in between certain limits of partial pressure of water and temperature. There seems little point in doing this for the results given here in any detail, but if one takes for example the data from Figure 4.3 for FPOL then, over the range 7-24 mm Hg at 30°C, the relationship between the frequency change and partial pressure of water is $\Delta f/kHz = 0.41$ /mm Hg. Whether this will be adequate to compensate for the effect of relative humidity on DMMP adsorption remains to be seen, and whether this would be useful in practice when one is trying to obtain a response over a very short timescale rather than a long one, has yet to be determined. There is reason from previous work by the author published elsewhere (see First Periodic Report) for optimism on this point where it was shown that in similar work, one could obtain better than 90% correction of the effect of water vapour on the response of piezoelectric crystal devices using simple correction algorithms in real time. This was over a relatively limited humidity range however and at a single temperature but there is every indication that the results obtained here demonstrate the viability of this approach for the FPOL and PVP crystals for DMMP determination.

6.   Conclusions

6.1   In this research programme the goal was to carefully measure the water adsorption isotherms onto selected coatings placed on surface acoustic wave devices. In order to achieve this the research group set about building equipment and establishing testing protocols that could be relied upon. This was considered absolutely necessary as one recognised the very long timescale involved in any experiment to do with measuring adsorption isotherms. The work involved in setting up the rig which was able to operate over a wide range of relative humidity and a range of temperatures was much more demanding than one had at first anticipated, even though it is well known how problematic these particular types of experiments are. Nonetheless, the endeavour has been worthwhile as the confidence one can place on the results obtained is great. Similarly, it was important to establish coating protocols for the SAWS in order to ensure a means of making a reproducible coating where the response characteristic was not significantly affected by the nature and uniformity of the coating. A great deal of effort went into this and although rather difficult to quantify the quality of coatings, some effort was made to achieve this. The trade-off between rate of evaporation of solvent and ease of application is clear and also the eventual conclusion that the best method involved use of a fine brush, is not something that one could easily have anticipated from a position of no experience in coating procedures. The design and construction of the RF oscillator is something which has received very little attention in previous work in the application of SAWS or piezoelectric crystals to chemical analysis. In this work a systematic study was undertaken of the oscillator design and has resulted in an oscillator of very high stability by any criterion. The combination of these studies has resulted in an experimental procedure which gives results of a definitive nature.

6.2   The experiments undertaken show clearly that one can relate the frequency change of the SAWS to the vapour pressure of water and relative humidity in the atmosphere at temperatures between 30 and 40°. Both FPOL and PVP, chosen for their particular response functions to water and DMMP, show significant response to water vapour as had been anticipated. The mechanisms of adsorption seems to change as one goes from low to high relative humidity, witnessed by the changes in gradient of the response curves. It is unfortunate that these breaks appear in the middle of the relative humidity range for these two particular compounds which have otherwise such good characteristics, as it makes the construction of a simple algorithm, particularly for PVP, problematic. The nature of these adsorption terms was discussed in some detail above (section 4 and 5). Of more importance than the exact shape of the curves, is the fact that in a real situation where conditions in the atmosphere may change rather rapidly, the response time of not only the SAWS but also the system associated with the SAWS, that is the prefilters, sampling system, etc., may take some significant time to respond. If the relative humidity was being sensed by an external device and the correction for the relative humidity thus calculated imposed upon the SAWS, then this would clearly give an erroneous response if the SAWS itself had not changed in the same way as the humidity sensor. It is important therefore for the SAWS itself to be the humidity sensor and for one side to correct the other. This is why dual sided SAWS have been proposed and devised. The problem then resolves itself to the fact that the PVP and FPOL have got different response functions to water vapour over the same partial pressure range. Figs.4.1 and 4.2   demonstrate this quite clearly and these are in accord with the data obtained previously in Periodic Reports 3 and 4. In a system which uses the response of one side (anticipated PVP in this case) to monitor mainly water vapour fluctuations and the other side (anticipated FPOL in this application) to monitor changes in the phosphonate concentration, the correction function is going to be quite complicated over a wide relative humidity

range. Figs. 4.1 and 4.2 show however that over a limited range say, from 10mm-24mm and coatings round 70 kHz, at 30°C, correction would be relatively straightforward.

6.3   Alternatively, one could use the other approach of trying to work down at very low relative humidities where the magnitude and also gradient of the response function is much smaller. In the past this has always been deemed very difficult because of the problem in removing water vapour whilst not removing the phosphonates which are notoriously sticky compounds and easily hydrolysed when adsorbed onto moist metallic surfaces. It will be possible, using the relatively recently exploited denuder tubes (which work is going on in this Department) to preconcentrate even unstable compounds like phosphonates onto specific surfaces and then dissolving the products of the adsorption under dry air conditions onto the SAW device. In this way, one is working in a regime where ambient relative humidity is rather low and, although one may not be determining directly the original target species, the specificity of the adsorption process in the preconcentrator and subsequent determination of the, for example hydrolysis product, will give an indication of the concentration of the target species. We have demonstrated this recently for nitrobenzene with some considerable success and concentrations in the ppb-ppt region.

6.4   In conclusion therefore, although the DMMP work has yet to be carried out, one can be reasonably confident that over a relatively limited range of humidities and temperatures, correction of the response of coated SAWS to water vapour can be achieved even though the adsorption mechanisms are possibly more complex than had at first been anticipated, or hoped for. Work is proceeding in the Department to obtain the data for DMMP and DIMP, as well as ancillary work on the compensation for temperature fluctuations to the uncoated SAWS output. Working with the Plessey Company in England, we have had designed and constructed a dual delay line SAWS with internal temperature sensor on the surface of the silica substrate. We have developed circuits to employ these delay lines in 70 MHz oscillators and also to measure the temperature as a function of the detector resistance. With the information on surface temperature, and the known adsorption/desorption characteristics of water vapour and DMMP from these surfaces, we will be able to make a working system within the next year or so. It is still probable, whatever the outcome of this work, that insufficient sensitivity will be achievable using the SAWS devices to permit useful application of the sensors for nerve agent determinations as the required concentrations are rather less than can be achievable with the SAWS device itself. It seems probable therefore that the best way to go is to use a preconcentration system which will have a number of different advantages, not only will it effect preconcentration of the agent but also permit desorption of the concentrated analyte into the SAWS under optimum conditions of temperature and low relative humidity. It is hoped to be able to continue and develop these ideas in future research projects.